



Influence of heat-treatment of Ketjen Black on the oxygen reduction reaction of Pt/C catalysts

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HIGHLIGHTS

- Enhancement of specific ORR activity by heat-treatment of a carbon black support in the temperature range 1000–2000 °C.
- Selective exposition of Pt(110) surface depending on the HTT.
- Correlation between the SOA and the fraction of Pt(110) exposition.

ARTICLE INFO

Article history:

Received 13 March 2012

Received in revised form

11 June 2012

Accepted 31 July 2012

Available online 8 August 2012

Keywords:

Oxygen reduction catalysts

Carbon

Platinum

Activity enhancement

PEFC

ABSTRACT

The influences of the heat-treatment of Ketjen Black EC300J in the temperature range 1000–2000 °C on the catalytic activity of loaded Pt for oxygen reduction reaction (ORR) were studied. A maximum enhancement in the specific ORR activities (SOA) was observed for the carbon heat-treatment at 1500 °C. The heat-treatment of carbon induced decreases in porosity and the development of graphitic structures; however, no direct correlations were observed between these properties and the SOA. Transmission electron microscopy and X-ray photoelectron spectroscopy, respectively, showed enhancements in the uniformity of the Pt particle size distribution and of the extent of surface reduction of Pt with increasing heat-treatment temperature (HTT). Cyclic voltammetry in 0.5 M H₂SO₄ aqueous solution detected changes in the hydrogen adsorption at 0.12 V vs. a reversible hydrogen electrode, depending on the HTT of the carbon support, and this was ascribed to hydrogen adsorption on the Pt(110) surface, the most active crystal face of Pt for ORR. The fraction of Pt atoms belonging to the (110) surface out of the total surface Pt atoms showed an excellent correlation with the SOA. Heat-treatment of the carbon support was therefore concluded to be an effective treatment for enhancing the SOA of Pt.

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1. Introduction

The cost of the cathode catalyst is a major obstacle to the commercialization of proton exchange membrane fuel cells (PEMFCs). Reduction of the amounts of Pt metal used is an urgent issue, which needs to be resolved [1,2]. Two reduction methods are available: (1) enhancement of the activities of Pt, for example, by finer dispersion of Pt [3], by alloying with other base metals [4–6], or by coating an active Pt layer on base metal core particles. [7], and (2) development of non-Pt cathode catalysts [8–15]. Finding other ways of increasing the activities of Pt is the most practical option.

Metal–support interaction is a key concept in modifying metal-supported catalysts. The extreme cases were found in Ni/TiO₂ and

Pt/TiO₂ systems, where the catalytic properties of the metal particles were greatly altered, i.e., strong metal–support interactions [16,17]. Even if the interaction is not strong, we can expect some interactions between metal particles and support materials to alter the properties of catalysts, since small nanometer-sized metal particles would be susceptible to the chemical or electronic influences of support materials [18].

The electronic properties and chemical structures of carbons vary, depending on the heat-treatment temperature (HTT) [19]. The catalytic properties of finely divided metal particles loaded on carbons with different heat-treatment histories will therefore be affected. We anticipated that heat-treatment of the carbon supports would improve the oxygen reduction reaction (ORR) activities of Pt particles. To the best of our knowledge, the influences of the heat-treatment of carbon supports have been studied with respect to avoidance of electrochemical corrosion during fuel-cell operation [20,21], but have never been studied from the

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perspective of modifying the catalytic properties of metal particles through the characteristics of the support materials. The objective of the present study is to clarify the influence of the heat-treatment of a carbon support material, carbon black, on the ORR activity of supported Pt particles.

2. Experimental

2.1. Sample preparation

Ketjen Black EC300J (Lion Corp.) was selected as the catalyst support to be heat-treated at different temperatures in the range 1000–2000 °C. The heat-treatments up to 1200 °C were performed under a nitrogen stream at 10 °C min⁻¹ for 1 h using an infrared image furnace (RHL-E410P, ULVAC Riko Co., Ltd.). Heat-treatments of the carbon supports at HTTs above 1200 °C were performed by reheat-treating the carbon treated at 1000 °C using a furnace equipped with a graphite heating element, operated under dynamic vacuum conditions. The untreated and heat-treated carbons are identified by their final HTT, for example, the untreated and 1000 °C-treated carbons are designated as EC30(UN) and EC30(1000), respectively.

The Pt catalyst was loaded onto the heat-treated carbons by impregnation from a Pt(NO₂)₂(NH₃)₂ ethanol solution prepared according to the following procedure. A nitric acid solution of Pt(NO₂)₂(NH₃)₂ (Ishifuku Metal Industry Co., Ltd.) was evaporated to dryness. The retrieved solid compounds (0.4 g on a Pt basis), a carbon support (0.6 g), and citric acid (2.0 g) were placed together in 320 g of ethanol (Wako Pure Chemical Industries, Ltd., 99.5%). The mixture was heated at 80 °C for 16 h under reflux conditions to obtain a Pt/C catalyst dispersion solution. The solution was filtered, rinsed with hot water, and dried at 80 °C with blown air for 16 h to retrieve the Pt/C catalyst. The nominal catalyst loading was 40 wt%. Hereinafter, the Pt catalysts loaded on the carbon supports are differentiated by the type of support, for example, the Pt catalyst supported on EC30(1000) is represented by Pt/EC30(1000).

2.2. Characterization

Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature using a BELSORP mini II (BEL Japan, Inc.) after evacuating the carbon supports at 110 °C for 1 h. The surface area (S_{BET}), micropore volume (V_{micro}), and mesopore volume (V_{meso}) were calculated using the Brunauer–Emmett–Teller (BET), Dubinin–Radushkevich (DR), and Dollimore–Heal (DH) methods, respectively. The calculated values are tabulated in Table 1. The Pt surface area was evaluated using CO pulse adsorption measurement equipment (R6015, Ohkura Riken) after reducing the sample in an H₂ stream for 1 h at 130 °C. The CO-surface areas ($S_{\text{Pt(CO)}}$) are shown in Table 2. Catalyst loading was determined gravimetrically. X-ray diffraction (XRD) was employed to evaluate the carbon structure and Pt crystallite size using a diffractometer (RINT 2100/

Table 2
Properties of the prepared Pt/C catalysts.

Catalyst	Pt loading (wt%)	$L_{\text{Pt}(110)}$ (nm)	$S_{\text{Pt(CO)}}$ (m ² g ⁻¹ pt ⁻¹)	$S_{\text{Pt(EC)}}$ (m ² g ⁻¹ pt ⁻¹)	ORR current density at 0.85 V (A m ⁻² pt ⁻²)
Pt/EC30(UN)	39.8	2.7	67	43	0.14
Pt/EC30(1000)	36.8	3.1	64	42	0.24
Pt/EC30(1200)	38.4	3.3	59	41	0.23
Pt/EC30(1500)	35.9	3.3	52	28	0.33
Pt/EC30(1800)	38.4	3.5	46	26	0.25
Pt/EC30(2000)	35.2	3.5	38	21	0.22

PC, Rigaku Corp.) equipped with a Cu-K α radiation source. Transmission electron microscopy (TEM) observations were conducted using a JEM2010 (JEOL Ltd.) instrument with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was used to determine the electronic states of the catalysts by observing the C1s and Pt4f photoelectron emissions with monochromatic Al-K α radiation (AXIS NOVA, Shimadzu Corp.).

2.3. Electrochemical methods

The working electrode was prepared using the method reported by Schmidt et al. [22], as follows: (1) A catalyst ink was prepared by dispersing 2.5 mg of Pt/C in a mixed solution of 300 μ L of ethanol, 300 μ L of water, and 25 μ L of 5% Nafion solution by sonication for 30 min. (2) The ink (4 μ L) was pasted onto a disk electrode ($\phi = 6$ mm) and then air-dried. The electrolyte and the reference electrode were a 0.5 M H₂SO₄ aqueous solution and a reversible hydrogen electrode (RHE), respectively. Cyclic voltammetry (CV) was performed by sweeping the electrode potential between 0.0 V and 1.0 V vs. RHE, at 50 mV s⁻¹, in the electrolyte, after purging the dissolved oxygen by nitrogen bubbling for 20 min. The obtained voltammograms are presented in Fig. 1(a). The electrochemical surface areas (ECSA, denoted as $S_{\text{Pt(EC)}}$) of Pt were calculated from the hydrogen adsorption waves observed in the potential range of 0.05–0.4 V vs. RHE, shown in Fig. 1(b). The $S_{\text{Pt(EC)}}$ values are tabulated in Table 2 with the surface areas obtained by CO adsorption ($S_{\text{Pt(CO)}}$). These two Pt surface areas were revealed to have a good correlation with a correlation coefficient of 0.94. Hereinafter, we employed the $S_{\text{Pt(EC)}}$ when we discussed the specific activity of Pt.

The ORR activity of the catalyst was evaluated using linear sweep voltammetry (LSV). The reference LSVs (N₂-LSVs) were obtained in a deaerated electrolyte by linearly sweeping the potential of the working electrode from 1.0 V to 0.0 V vs. RHE at 1 mV s⁻¹ with a disk electrode rotating at 1500 rpm. The LSVs (O₂-LSVs) were measured in an oxygen-saturated electrolyte, after oxygen bubbling for 20 min. Finally, net voltammograms for the ORRs were obtained by subtracting the N₂-LSVs from the O₂-LSVs.

3. Results and discussion

3.1. Electrochemical oxygen reduction reaction activity

Fig. 2 shows linear sweep voltammograms of the prepared Pt/C catalysts in a 0.5 M H₂SO₄ solution. The ordinate represents the current density normalized by the ECSA, $S_{\text{Pt(EC)}}$, listed in Table 2. It can be observed that the ORR activity of Pt supported on carbons subjected to different heat-treatments varies, depending on the HTT. With increasing HTT, up to 1500 °C, the ORR activity increased; however, heat-treatment at 2000 °C resulted in a decrease in the activity. This indicates that the heat-treatment of the carbon supports can alter the catalytic properties of loaded Pt catalysts.

Table 1
Properties of the carbon substrates.

Support material	Heat-treatment temperature (°C)	Nitrogen adsorption			XPS	
		S_{BET} (m ² g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	$x_{\text{C-O}}$	$f_{\text{sp}^1/\text{sp}^2}$
EC30(UN)	N/A	753	0.133	1.15	0.36	0.61
EC30(1000)	1000	742	0.126	1.26	0.19	0.45
EC30(1200)	1200	687	0.112	1.26	0.27	0.50
EC30(1500)	1500	396	0.086	1.39	0.19	0.44
EC30(1800)	1800	243	0.055	1.29	0.17	0.50
EC30(2000)	2000	194	0.054	1.43	0.17	0.39

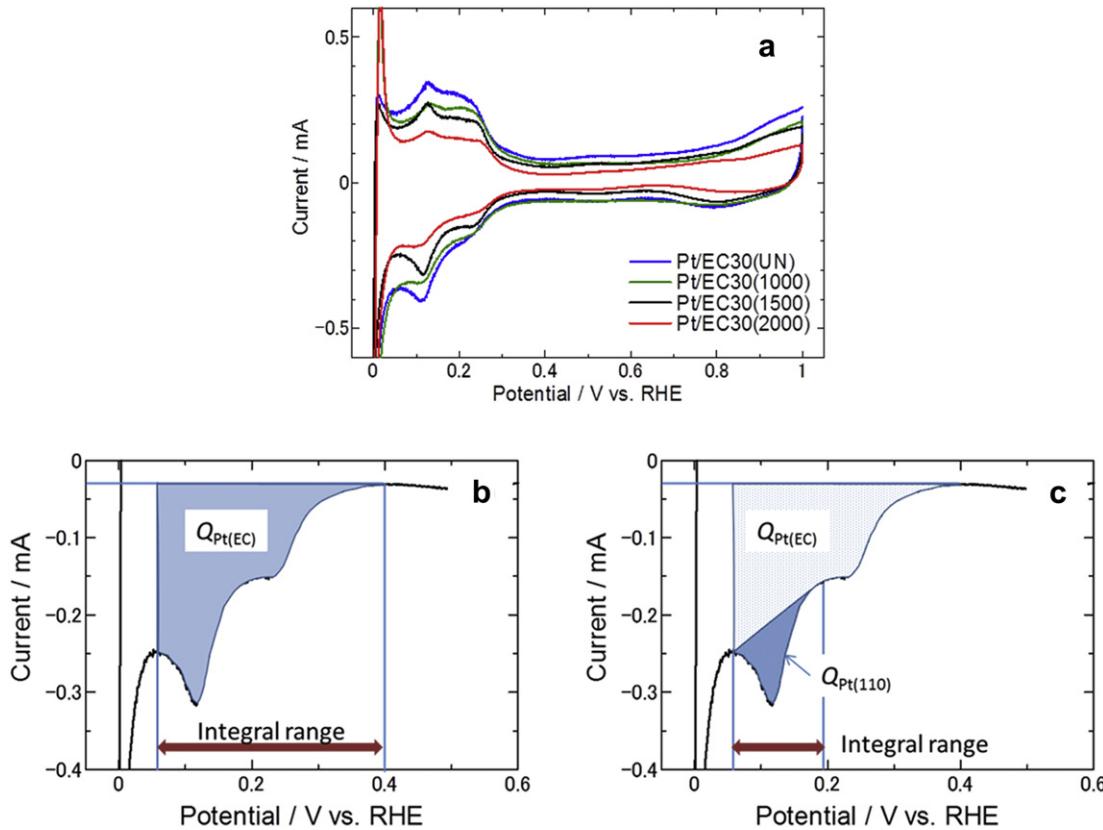


Fig. 1. (a)Cyclic voltammograms of Pt/C catalysts measured in 0.5 M H_2SO_4 aqueous solution. (b) and (c) are the diagrams showing how to calculate the charges related to $S_{\text{Pt}(\text{EC})}$ and $S_{\text{Pt}(110)}$, respectively.

For quantitative comparison of the activities of the Pt particles supported on the carbons, we introduced the specific ORR activity (SOA), which is defined as the current density at 0.85 V vs. RHE in the LSVs shown in Fig. 2. Fig. 3 shows the relation between SOA and HTT. SOA increased with increasing HTT up to 1500 °C, and then decreased above this temperature. The maximum improvement in the SOA was achieved by heat-treatment at 1500 °C, where the SOA was 2.4 times higher than that of a reference, Pt/EC30(UN). The SOA should be constant, regardless of the HTT of the carbon support, if the platinum particles have an identical active site regardless of the

type of the carbon supports. Therefore we guess that the properties, such as electronic or crystallographic states of the active sites on the Pt particles vary, depending on the HTT of the carbon support.

3.2. Properties of carbon supports

The BET surface areas (S_{BET}), micropore volumes (V_{micro}), and mesopore volumes (V_{meso}) are shown in Table 1. The S_{BET} and V_{micro} values of the carbon supports rapidly decreased above an HTT of

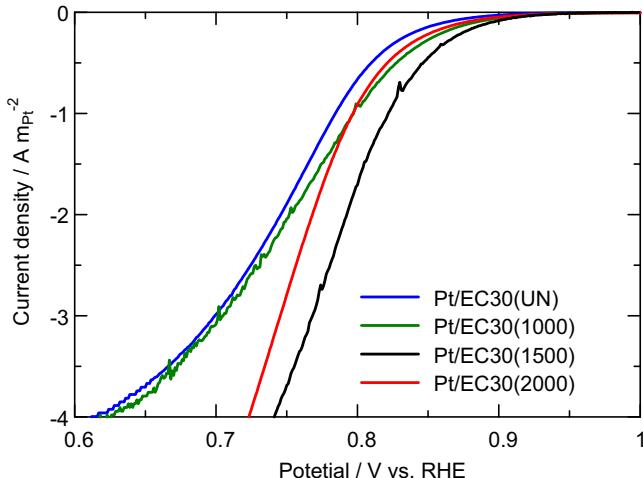


Fig. 2. Linear sweep voltammograms of Pt/C catalysts for different heat-treatment temperatures of carbon substrates.

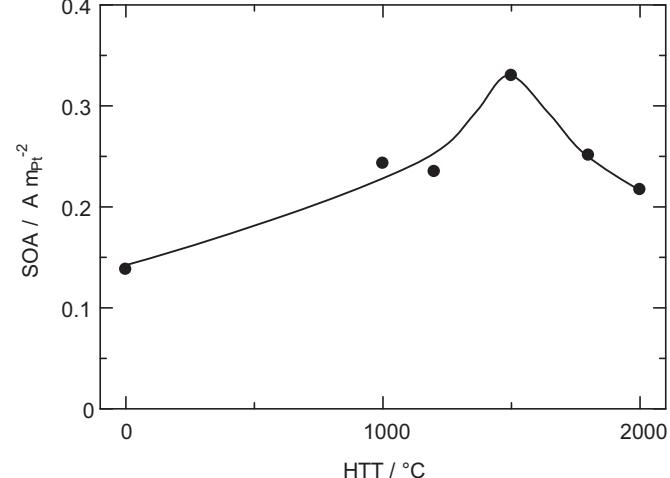


Fig. 3. Dependence of specific oxygen reduction reaction activity of Pt/C catalysts on heat-treatment temperatures of carbon supports.

1200 °C, whereas V_{meso} increased slightly. In general, lowering the BET specific surface area of the supports gives rise to a decrease in the surface area of the metal particles.

Diamond analysis is a method used to obtain the distribution of graphitic crystallites size in their a -axis direction (L_a) from the (11) peak, which is a two-dimensional X-ray diffraction observed for non-graphitized (turbstratic) carbons [23]. Fig. 4 shows the distribution histograms of L_a , analyzed using a software package (Carbon Analyzer, DiHiGa, Ryoka Systems Inc.) [24]. Heat-treatment up to 1500 °C increased the fraction above 4 nm at the expense of the fraction below 2 nm, but the latter is still predominant. Heat-treatment above 1500 °C induced further increases in the fraction above 4 nm.

C1s XPS measurements revealed that the chemical states of the carbon supports changed with HTT, as shown in Fig. 5. An increase in HTT resulted in narrowing of the main electron emission, located at 284.5 eV, and a decrease in the higher binding energy (BE) envelope region. To obtain further information, the spectra were divided into five sub-spectra, i.e., three surface oxygen functional groups (C—O at 286.0 eV, C=O at 287.3 eV, and COOH at 289.3 eV) and two carbon atoms in different hybridized states (sp^3 at 285.3 eV and sp^2 at 284.3 eV) [25,26]. The decrease in electron emission in the higher BE region was apparently caused by the thermal elimination of oxygen functional groups; the total numbers of oxygen functional groups are presented as $x_{\text{C}-\text{O}}$ in Table 1. The narrowing of the main C1s peak was caused by a decrease in the sp^3 -hybridized carbon atoms upon heat-treatment. The presence of sp^3 carbon atoms indicates the presence of defects in the graphitic structure, the number of which decreased with HTT, shown as $f_{\text{sp}^3/\text{sp}^2}$ in Table 1. This may affect the early stage of the crystal growth of Pt particles.

3.3. Dispersion of Pt particles

Fig. 6 shows TEM images of the catalysts. Pt/EC30(UN) showed finely dispersed Pt particles with diameters in the range

1.7–3.3 nm. Increasing the HTT up to 1500 °C eliminated the smaller Pt particles. The heat-treatment at 2000 °C induced significant aggregation of the Pt particles, giving a non-uniform distribution, along with crystallization of the carbon support. Fig. 7 compares the size distribution histograms of the catalysts; these were obtained by counting 200 particles, in order to obtain more quantitative information on the Pt particle size. The increase in the HTT did not cause significant increases in the average particle size up to 1500 °C; however, the standard deviation (SD) decreased. Heat-treatment at 2000 °C caused increases in both the average size and the SD. A decrease in SD indicated an increase in the uniformity of the Pt particle size distribution, meaning that such carbon supports might have larger numbers of sites for the deposition of Pt particles.

3.4. Pt surface states

Fig. 8 shows the Pt4f XPS spectra of the prepared catalysts, which comprise two photoelectron emission bands, i.e., $4f_{5/2}$ at 71.5 eV and $4f_{7/2}$ at 74.8 eV. In the following discussion, we employed the $4f_{7/2}$ bands. The spectra indicated that the major Pt species were in the metallic state (BE = 71.4 eV, $\text{Pt}4f_{7/2}$, BE = 74.7 eV, $\text{Pt}4f_{5/2}$); however, there were slight increases in the abundance of the species with higher BE than the metallic species, i.e., 71.4–73.8 eV region. The intensities of the species corresponding to the higher BE emissions decreased with increasing HTT. The states in the BE region observed for Pt/EC30(UN) vanished until an HTT of 1000 °C. The interpretation of the higher BE contributions to the Pt XPS spectra has been discussed. Liu et al. interpreted them as the oxidized Pt surface [27], whereas Takasu et al. explained them in terms of Pt particle size effects [28]. Whatever the interpretation of the higher BE contribution is, the chemical or electronic states of the Pt particles are influenced by the type of carbon support.

Cyclic voltammograms of the Pt/C catalysts shown in Fig. 1(a) have similar shapes, but significant differences are observed in the

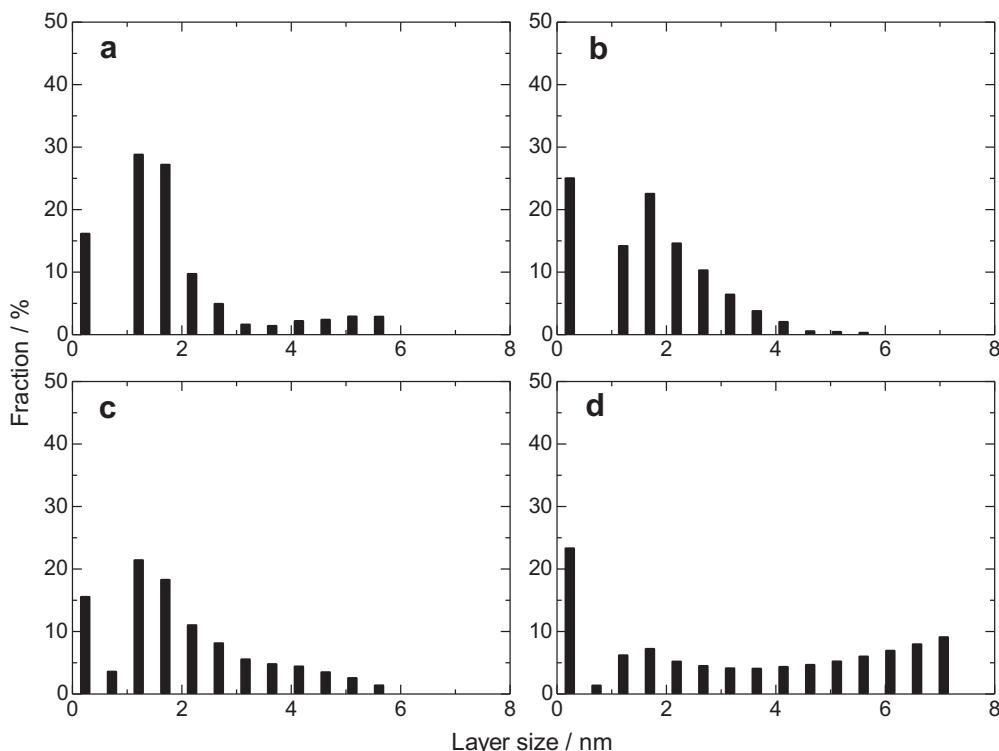


Fig. 4. Histograms of a -axis crystallite size distribution obtained by diamond analysis: (a) EC30(UN), (b) EC30(1000), (c) EC30(1500), and (d) EC30(2000).

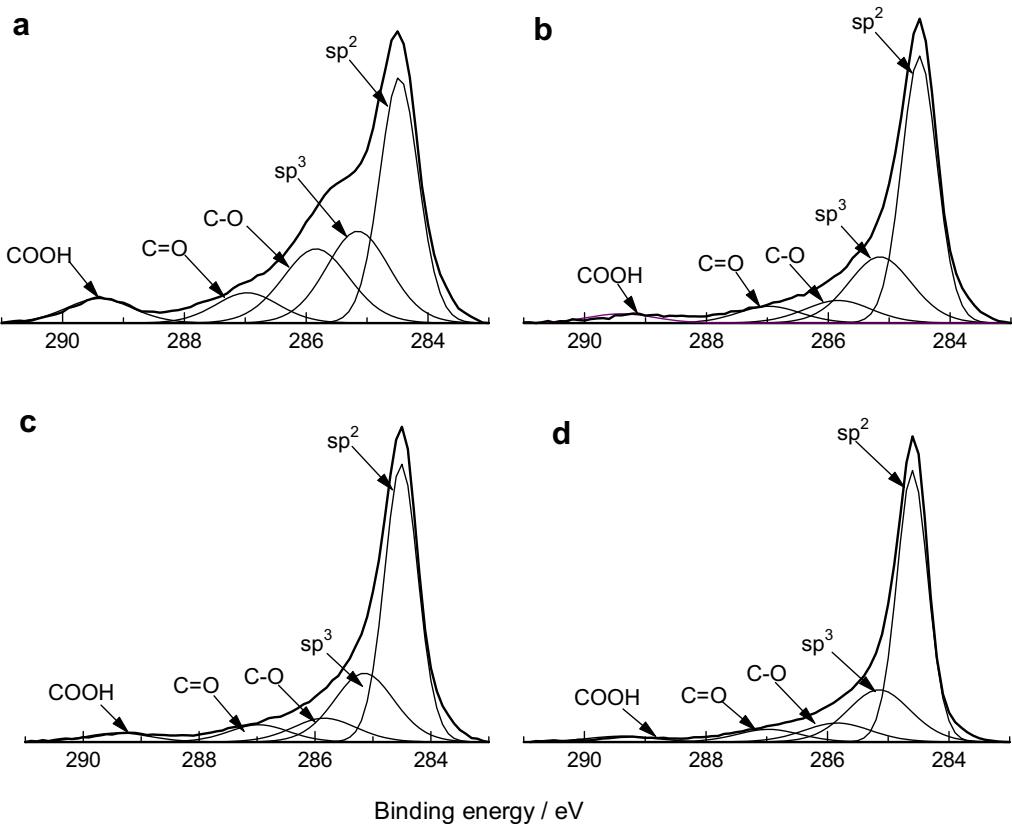


Fig. 5. C1s X-ray photoelectron spectra of carbon supports heat-treated at different temperatures: (a) EC30(UN), (b) EC30(1000), (c) EC30(1500), and (d) EC30(2000).

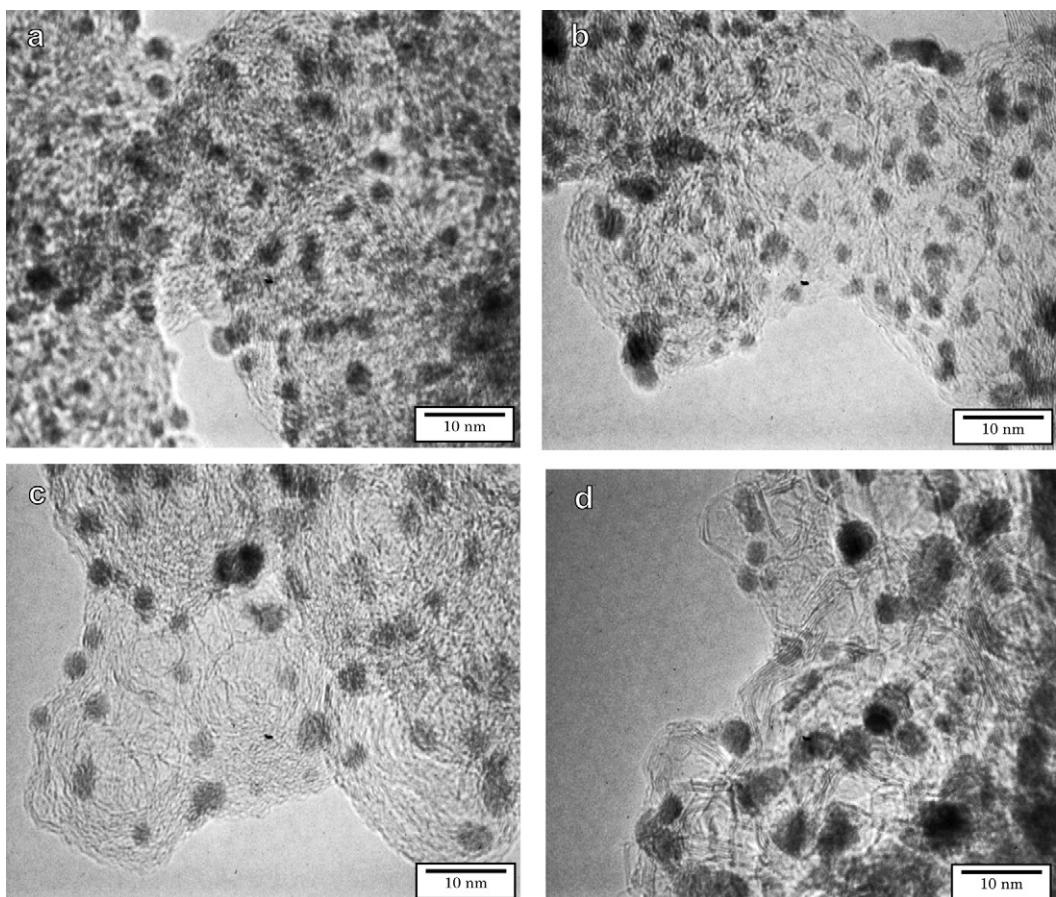


Fig. 6. Transmission electron micrographs of Pt/C catalysts: (a) Pt/EC30(UN), (b) Pt/EC30(1000), (c) Pt/EC30(1500), and (d) Pt/EC30(2000).

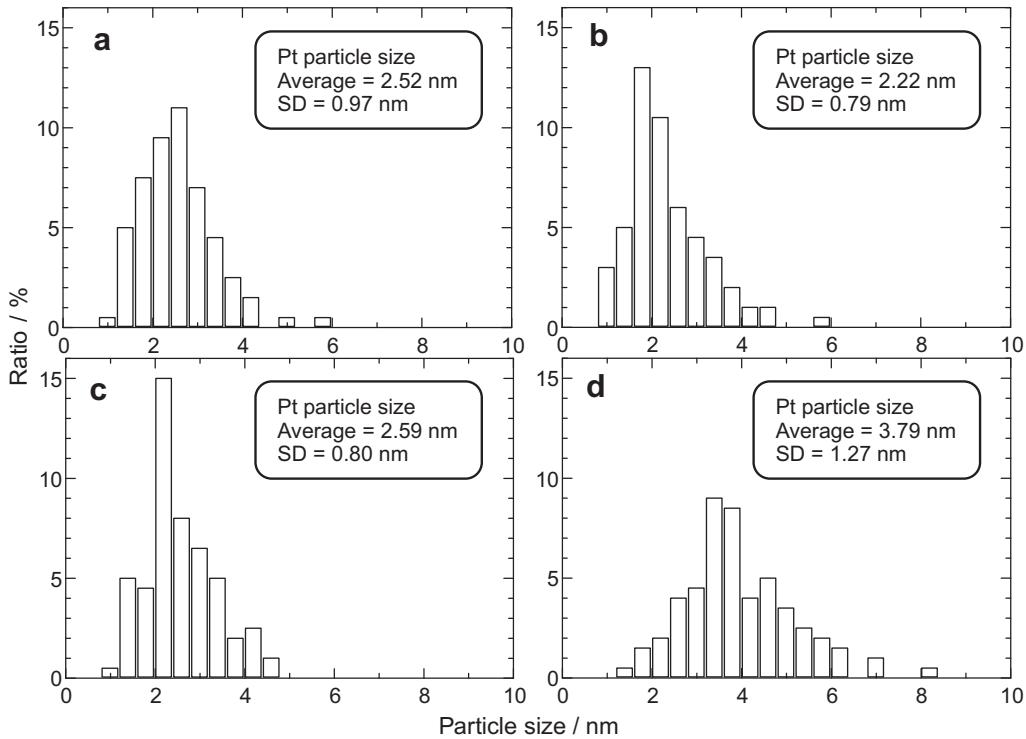


Fig. 7. Histograms of Pt particle size on carbon supports heat-treated at different temperatures: (a) Pt/EC30(UN), (b) Pt/EC30(1000), (c) Pt/EC30(1500), and (d) Pt/EC30(2000).

adsorption peak at 0.12 V, i.e., its intensity changed depending on the carbon HTT. Furuya et al. conducted a cyclic voltammetric study of single Pt crystals with different crystal faces and found that the hydrogen adsorption potentials depended on the type of crystal face [29]. According to their interpretation, the characteristic peak at 0.12 V could be assigned to the hydrogen adsorption wave resulting from Pt(110). The ratios of the charges corresponding to the Pt(110) peak were evaluated in the manner shown in Fig. 1(c). First, the contribution of (110), indicated by dark color, was separated from the main body of the hydrogen adsorption wave, which was used for calculating $S_{\text{Pt}(\text{EC})}$ in Fig. 1(b). The ratios of the former contribution to the latter contribution were calculated for the catalysts and plotted against the HTT of the carbon support (Fig. 9). The ratio increased with increasing HTT up to 1500 °C, and then

decreased; this behavior is quite similar to the behavior of the SOA with respect to HTT (Fig. 2). The changes in the SOA with heat-treatment of the carbon support are therefore concluded to be the result of changes in the fraction of Pt(110).

Cubo-octahedral structure is a model structure of small Pt particles, which has been employed in theoretical studies on the relation between particle size and the different surface sites. The representative structure of Pt particles consists of eight (111) and six (100) crystallographic faces bounded by edge and corner atoms. Since the structure is a stable structure of face-centered cubic crystals such as Pt [30], the presence of Pt(110) crystal planes seems to be unrealistic. However, R. van Hardeveld and Hartog threw doubt on the formation of crystals of equilibrium shape under the

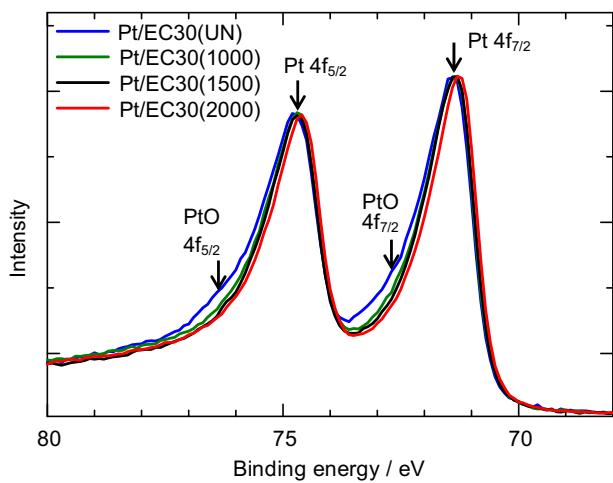


Fig. 8. Pt4f X-ray photoelectron spectra of prepared Pt/C catalysts.

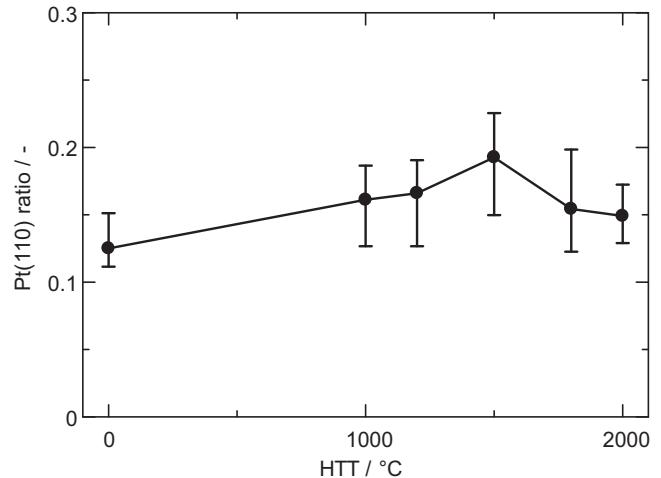


Fig. 9. Dependence of fraction of exposed Pt(110) atoms on heat-treatment temperature.

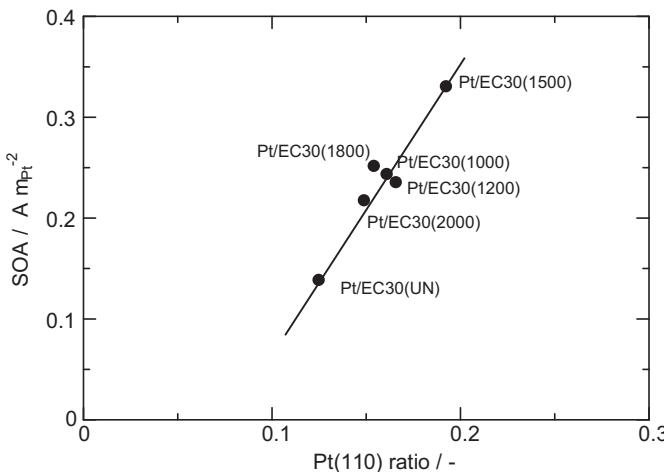


Fig. 10. Relationship between specific oxygen reduction reaction activity and fraction of exposed Pt(110) atoms.

usual preparation conditions, since they observed only asymmetric shapes unlike the crystals in equilibrium [31]. Moreover, different shapes of Pt nanoparticles other than cubo-octahedral structure has been prepared by controlling the conditions such as proper selections of surfactants [32]. The above arguments rationalize our inference of the presence of Pt(110) by taking into account of the influences of the carbon supports.

Different ORR activities for the different crystal planes of Pt were reported by Markovic et al., who determined the order of the ORR activities to be as follows: Pt(110) >> Pt(111) > Pt(100) [33]. A good correlation was observed between the SOA and Pt(110) ratio, as shown in Fig. 10. This clearly suggested that exposure of Pt(110) is the determining factor in the ORR activities of the catalysts. Furthermore, appropriate heat-treatments of the carbon supports induced selective exposure of the most active Pt surface, Pt(110). However, we do not know the mechanism by which a higher fraction of the Pt(110) plane is exposed because of heat-treatment of carbon support.

4. Conclusion

In this study, we investigated the influences of the heat-treatment of a carbon substrate on the properties of Pt in Pt/C catalysts for PEMFCs. Heat-treatment of the carbon support changed the SOA of Pt loaded on the support; the maximum SOA was obtained when a substrate treated at 1500 °C [EC30(1500)] was used as the catalyst support. The mechanism of the enhanced activity was explained by involvement of a particularly active crystal plane, Pt(110); this was supported by the appearance of H₂-adsorption peaks in cyclic voltammetry. The heat-treatment of the carbon support was therefore shown to be important in the

enhancement of ORR activity by growth of active Pt crystal planes. The remaining issue is to characterize the mechanism of elective crystal plane growth because of the heat-treatment of carbon.

Acknowledgment

The authors thank Ms Yukiko Sayama for preparing the manuscript and illustrations.

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